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Abstract

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On the Influence of an Electric Field on the Development of Porosity during Interdiffusion in Alkali-Halide Single Crystals

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1. Numerous experiments with specimens composed of mutually soluble metals have reliably established that diffusion homogenization, which in the general case takes place when the partial diffusion coefficients of the components are unequal, is accompanied by two effects that are expressed the more clearly the greater the difference in the partial diffusion coefficients (1). One of these effects—the so-called Kirkendall effect—consists in the displacement of the initial contact boundary between the components of the diffusion couple, marked by inert markers. The second consists in the nucleation and development of so-called diffusion porosity in that component of the couple from which, owing to the larger value of the corresponding partial diffusion coefficient, more atoms leave than enter. This effect, which is a direct consequence of the vacancy mechanism of diffusion, has been called in the literature the Frenkel effect (2).

It was shown earlier (3) that during interdiffusion in alkali-halide single crystals pores of diffusion origin also arise. In particular, active pore formation is observed in a KBr single crystal annealed in contact with a KCl single crystal. Both in metallic specimens and in specimens composed of alkali-halide single crystals, the development of diffusion porosity can be formally described as a consequence of the presence of a predominant flux of vacancies into that component of the diffusion couple in which the development of porosity is observed.

On the basis of general considerations, taking into account that in alkali-halide crystals vacancies are electrically charged, one may suppose that an externally applied electric field, by affecting the flux of charged vacancies, will influence the kinetics of the pore-formation process. In the general form stated above, this supposition should be valid irrespective of whether the direction of the external field coincides with the direction of the predominant vacancy flux or is opposite to it.

In the present article we set forth the results of experiments in which an effect of an externally applied field on the kinetics of development of diffusion porosity was found.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

2. The system KCl—KBr was chosen as the object of investigation. The idea of the experiments carried out was as follows.

In choosing the experimental procedure* it is necessary to bear in mind that, as was established earlier (^{4}), nucleation of pores, as a rule, takes place at various kinds of microdefects and impurities and, in particular, in the KCl—KBr system (^{3,5}) near-surface cracks and dislocations play a significant role. Since the distribution and density of defects in different specimens may differ to an extent sufficient to mask the effect of the field, the experiments were carried out on three-layer specimens KBr—KCl—KBr. In this case the two KBr plates were the two halves of a crystal split in half. The layer—

* The experiments were carried out with the participation of the diploma student L. Reznik.

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Fig. 1. Structure of the diffusion zones in KBr (+) and KBr (—), separated by an interlayer of KCl. $T = 650^{\circ}$, $t = 3$ hours; $E \simeq 200$ V/cm; 550×

Fig. 2. Sections of porous zones in KBr (+)—a and KBr (—)—b, parallel to the contact plane.
$T = 650^{\circ}$; $t = 3$ hours; $E \simeq 200$ V/cm; 630×

The KCl layer was obtained by evaporation in vacuum onto both KBr plates simultaneously. Specially designed experiments established that the character of pore formation in KBr single crystals in contact with a KCl single crystal or with a KCl layer obtained by condensation from the gas phase is essentially no different. The main experiments were carried out with deposited layers because, with this method, the contact at the KCl—KBr boundary is more perfect. The thickness of the KBr plates was $\simeq 3$ mm, and the total thickness of the KCl interlayer was $\simeq 300 \div 400$. The area of the three-layer specimen was $\simeq 1$ cm^2. To ensure reliable contact with the electrodes, nickel layers with a thickness on the order of fractions of a micron were deposited by evaporation in vacuum onto the free surfaces of the KBr plates. The electrodes were made in the form of massive nickel disks, to which current and potential leads were spot-welded; the upper disk lay freely on the surface of the specimen.

Fig. 3. Distribution functions of the quantities V_+/V_-; 1 —annealing without a field, 2 —annealing in a field $E \simeq 200$ V/cm, $T = 650^{\circ}$; $t = 3$ h

In an experiment with the described three-layer specimen, the identity of all

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

conditions (temperature, field magnitude, structural state of the specimens, annealing time) at the KCl—KBr boundaries is guaranteed, with the essential difference that at one of the boundaries the field must promote a predominant vacancy flux, whereas at the other it must hinder it to the same extent (of course, only so long as pore formation in one of the crystals is not suppressed by the field).

The main experiments were carried out at a temperature of 650°, which is $\sim 100^\circ$ below the temperature of "contact melting." Fields of the order of 100 V/cm were used; the applied potential difference was kept constant throughout the entire annealing (3 h).

Fig. 4. Dependence of the displacement of the maximum of the distribution function of the quantities V_+/V_- on the field. $T = 650^\circ$, $t = 3$ h

Figure 1 presents microphotographs of the structure of two diffusion zones separated by a KCl interlayer; in making the photomontage, the width of the KCl interlayer was reduced. In reality it always substantially exceeded the width of the diffusion zone.

3. As follows from Fig. 1, the total volume of pores located in the KBr single-crystal plate that was under positive potential substantially exceeds the pore volume in the plate that was under negative potential. It must be emphasized that this difference in volumes is not a consequence of a difference in the number of pores. Figure 2, which shows the structures of the porous regions in KBr(+) and KBr(−), indicates that, consistent with the identical initial defectiveness of these crystals, the pore density is approximately the same ($n \simeq 10^6$ pores/cm^2); however, the pores in KBr(+) are elongated in the direction of the concentration gradient, which leads to the noted difference in volumes.

The effect of the field on pore formation is conveniently represented graphically in the form of the curves in Fig. 3, where, on a semilogarithmic scale, curves are plotted for the distribution of the number of ratios of the pore volume in KBr(+)—V_+—to the pore volume in KBr(−)—V_-, as a function of the magnitude of this ratio.

Along the ordinate axis in Fig. 3 is plotted the probability (W) of encountering the logarithm of the ratio V_+/V_- of a given value. The statistics of the data needed to construct such curves were obtained as follows: in both diffusion zones, 20 sections of equal length were chosen arbitrarily, on which the quantities V_+

and V_- were determined; on the basis of these measurements, 400 dimensionless ratios V_+/V_- were compiled, using which the curves in Fig. 3 were constructed. The displacement of the maximum on the curve corresponding to the experiment carried out in the field is a quantitative measure of the effect being studied. As the experiments show, the magnitude of this displacement depends on the field and, in the range of fields investigated by us, proves to be approximately proportional to the magnitude of the field (Fig. 4).

4. It is necessary to draw attention to two fundamentally important features of the curves shown in Fig. 3. The first of these features is that, although the displacement of the maximum on curve 2 indicates that the field promotes the development of pores in KBr(+), the "tail" of the curve also extends into the region of ratios $V_+/V_- < 1$. This circumstance is a consequence of the statistical nature of the effect, i.e., of the sensitivity of the pore-formation process to the presence and magnitude of defects existing in the diffusion zone.

The second feature consists in the fact that the distribution curve corresponding to the experiment carried out in the field is more "smeared out," which should not have occurred, with the chosen method of constructing the curves, if the field promoted equally the growth of all pores located in KBr(+). The smearing of the distribution curve evidently indicates that in the diffusion zone, permeated by a network of defects and macroscopic pores, the equipotential surfaces are not parallel to the contact surface between the crystals, normal to which the pores grow. The basis for a joint discussion of curves 1 and 2 (Fig. 3) is that in both specimens the pore density was practically the same and the specimens were prepared simultaneously under identical conditions.

A discussion of the mechanism of the effect described and of its dependence on the physical constants of the contacting single crystals will be the subject of a separate article.

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